



REPORT DOCUMENTATION

1a REPORT SECURITY CLASSIFICATION Unclassified				3 DISTRIBUTION AVAILABILITY OF REPORT Approved for public release and sale; distribution unlimited.			
2a SECURITY CLASSIFICATION AUTHORITY				5 MONITORING ORGANIZATION REPORT NUMBER(S) 4135010			
2b DECLASSIFICATION/DOWNGRADING SCHEDULE MAY 14 1993							
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Report #23							
6a NAME OF PERFORMING ORGANIZATION University of Minnesota		6b OFFICE SYMBOL (If applicable) ONR		7a NAME OF MONITORING ORGANIZATION Office of Naval Research			
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry 207 Pleasant St. SE Minneapolis, MN 55455-0431				7b ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000			
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (If applicable) ONR		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N001489J1301			
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 2217-5000				10 SOURCE OF FUNDING NUMBERS			
				PROGRAM ELEMENT NO 61153N	PROJECT NO 4135	TASK NO	WORK UNIT ACCESSION NO 4135010
11 TITLE (Include Security Classification) "Hydrogen-Bond Polymorphs of Guanidinium 4-Biphenylsulfonate" (Unclassified)							
12 PERSONAL AUTHOR(S) Russell, V.A.; Etter, M.C.; Ward, M.D.							
13a TYPE OF REPORT Technical		13b TIME COVERED FROM 6/1/92 TO 5/31/93		14 DATE OF REPORT (Year, Month, Day) April 22, 1993		15 PAGE COUNT 7	
16 SUPPLEMENTARY NOTATION							
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)				
FIELD	GROUP	SUB-GROUP					
07	03		guanidinium sulfonate/hydrogen bonding/polymorphism				
19 ABSTRACT (Continue on reverse if necessary and identify by block number)							
<p>Hydrogen bonding is used to direct guanidinium sulfonates, $[\text{C}(\text{NH}_2)_3]^+\text{RSO}_3^-$, into specific molecular packing arrangements in the solid state. Guanidinium sulfonates frequently self-assemble into two-dimensional sheets formed by hydrogen bonds between the six guanidinium protons and the six sulfonate oxygen lone electron pairs. Guanidinium 4-biphenylsulfonate crystallizes in two polymorphic forms, differing only slightly in their hydrogen bonding patterns. We report on the synthesis of these polymorphs and their characterization by FTIR spectroscopy and single crystal X-ray diffraction.</p>							
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS				21 ABSTRACT SECURITY CLASSIFICATION Unclassified			
22a NAME OF RESPONSIBLE INDIVIDUAL Harold E. Guard				22b TELEPHONE (Include Area Code) (202) 646-4311		22c OFFICE SYMBOL ONR Code 1113	

OFFICE OF NAVAL RESEARCH

Grant or Contract N001489J1301

R&T Code 4135010

Technical Report #23

"Hydrogen-Bond Polymorphs of Guanidinium 4-Biphenylsulfonate"

by

V.A. Russell, M.C. Etter, and M.D. Ward


**University of Minnesota
Department of Chemistry
Minneapolis, MN**

April 22, 1993

**Reproduction in whole or in part is permitted for any purpose of the United
States Government**

**This document has been approved for public release and sale; its distribution
is unlimited.**

93 5 11 16 3

93-10496


Guanidinium 4-biphenylsulfonate was prepared as part of an investigation of the molecular packing modes of guanidinium with aryl sulfonates, $C_6H_5-(C_6H_4)_x-SO_3^-$, $x = 0$ to 3. Guanidinium crystallizes with 4-biphenylsulfonate in two polymorphs (by slow evaporation) as determined by IR spectroscopy. Elemental analysis confirms that the two polymorphs have identical chemical compositions and that neither is a solvate. Polymorph I crystallizes as light tan needles from equimolar solutions of guanidine hydrochloride and 4-biphenylsulfonic acid in cosolvent mixtures of methanol with acetone, acetonitrile, or ethyl acetate. Polymorph II, light tan thin squarish plates, is obtained from methanol or methanol/toluene solutions. In some cases both polymorphs were isolated from the same solutions.

Infrared spectra of the two polymorphs are distinct, with major differences occurring in the N-H stretching region $\sim 3400-3100\text{ cm}^{-1}$ and in the N-H bending region $\sim 1700-1600\text{ cm}^{-1}$. In polymorph I, N-H stretching bands occur at 3404, 3354, 3260, and 3190 cm^{-1} with one N-H bending band at 1652 cm^{-1} . The N-H stretching bands in polymorph II occur at 3469, 3344, 3259 and 3184 cm^{-1} with two N-H bending bands at 1698 and 1656 cm^{-1} . The high wavenumber bands at 3369 and 1698 cm^{-1} in polymorph II are indicative of non-hydrogen-bonded N-H. It is interesting to note that both polymorphs have nearly identical melting points of $274-275^\circ\text{C}$ (polymorph I) and $273.5-274.5^\circ\text{C}$ (polymorph II).

The single crystal X-ray structure of polymorph II was solved. The X-ray structural data follows: $C_{13}H_{15}N_3O_3S$, $M_r = 293.34$, triclinic, $P\bar{1}$ $a = 6.213(4)$, $b = 7.132(2)$, $c = 15.924(3)\text{ \AA}$, $\alpha = 85.63(2)$, $\beta = 80.93(3)$, $\gamma = 85.19(4)^\circ$, $V = 692.9(9)\text{ \AA}^3$, $Z = 2$, $D_c = 1.406\text{ g/cm}^3$, $\lambda(\text{Mo K}\alpha) = 0.71069\text{ \AA}$, $\mu = 2.32\text{ cm}^{-1}$, $F(000) = 308$, $T = 297\text{ K}$, $R = 0.040$, $R_w = 0.048$ for 2746 observed reflections. The structure is composed of hydrogen bond ribbons having four of the usual guanidinium-sulfonate hydrogen bonds linked into sheets by one other guanidinium-sulfonate N-H...O hydrogen bond and one guanidinium-sulfonate weak interaction; the sheets pack with a bilayer structure (Figure 1). The hydrogen bond pattern found in polymorph II (Figure 2) differs from the fully hydrogen-bonded pattern found previously in other guanidinium sulfonates in which the ribbons are linked by two hydrogen bonds through translation in two directions, rather than one. These two modes of packing of ribbons are illustrated schematically in Figure 3. Hydrogen bonds in polymorph II range in N...O length from 2.85 to 3.00 \AA (average 2.92 \AA) with N-H...O angles from 163 to 176° (average 169°). The guanidinium-sulfonate weak interaction has a N...O distance of 3.07 \AA and N-H...O angle of 122° .

For	
<input checked="" type="checkbox"/>	
<input type="checkbox"/>	
<input type="checkbox"/>	
City Codes	
and/or	
Dist	Special
A-1	

Preliminary X-ray data for polymorph I follows: $C_{13}H_{15}N_3O_3S$, $M_r = 293.34$, monoclinic, $C2/m$, $a = 32.56(2)$, $b = 8.161(8)$, $c = 10.457(5)$ Å, $\beta = 99.90(4)^\circ$, $V = 2737(6)$ Å³, $Z = 8$, $D_c = 1.423$ g/cm³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $T = 297$ K, $R = 0.143$, $R_w = 0.186$ for 1640 observed reflections. Views of crystal packing diagrams (Figure 4) show that the salt has a bilayer structure. Although the structure has not been refined and has a large error at this time ($R = 14\%$), we are reasonably confident that the hydrogen bond pattern in polymorph I is the usual fully hydrogen-bonded type, as in Figure 1b. IR spectral data supports this conclusion since the N-H stretching bands in polymorph I occur at wavenumbers consistent with hydrogen-bonded N-H. The two hydrogen-bond polymorphs presented here give new insight into the molecular packing modes of guanidinium sulfonates and will be useful in the further studies of these salts.

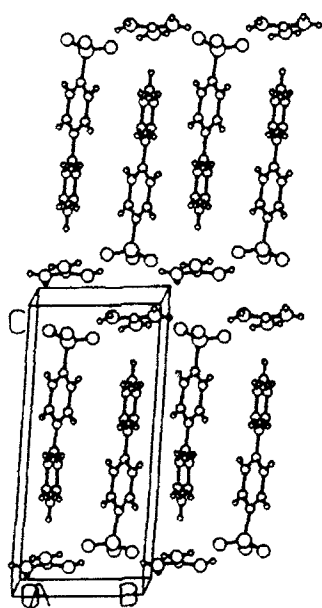


Figure 1. View along the a -axis of polymorph II showing the bilayer structure.

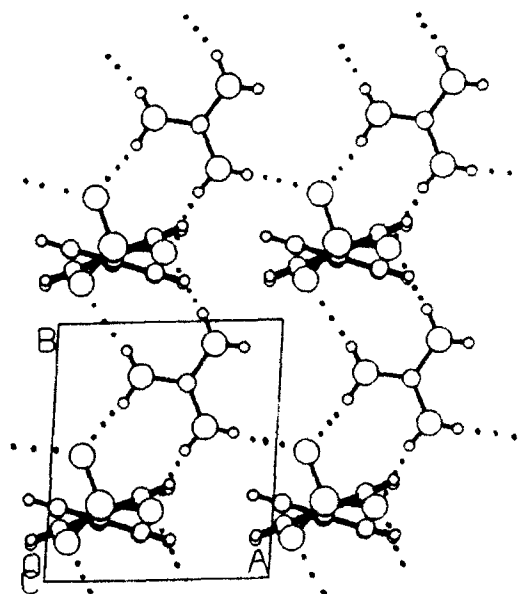


Figure 2. View along the c -axis of polymorph II showing one hydrogen-bonded sheet (hydrogen bonds indicated by dotted lines).

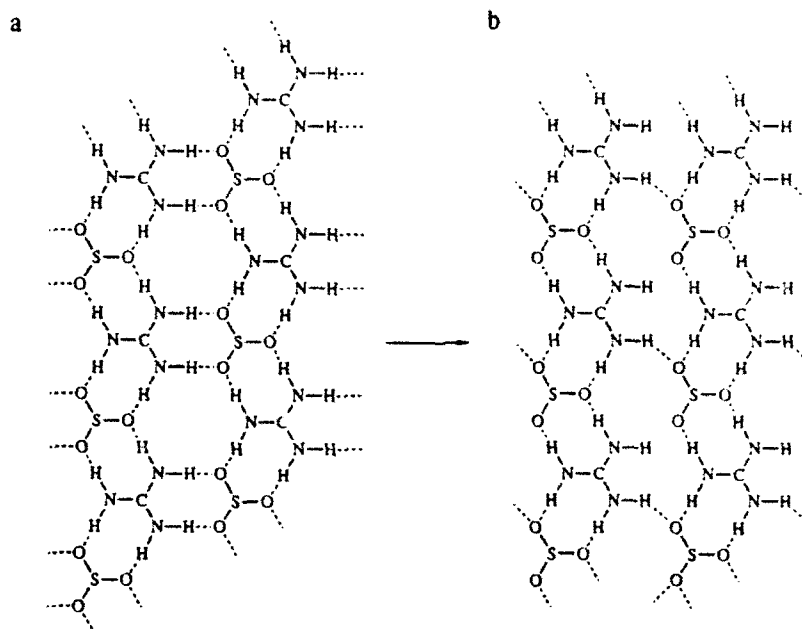


Figure 3. Schematics of two-dimensional hydrogen-bond arrangements in guanidinium sulfonates. (a) Common motif found previously and expected motif for polymorph I. (b) Motif found in polymorph II.

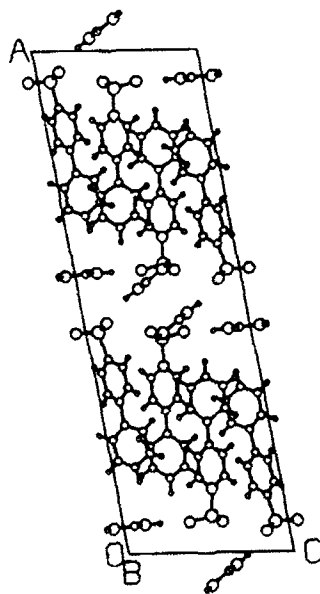


Figure 4. Preliminary view along the *b*-axis of polymorph I. Note that the refinement of the structure is not complete and the guanidinium ions are not in the correct orientation.

ORGANIC CHEMISTRY & MOLECULAR RECOGNITION - Distribution List

Professor O.T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Alan Berry
Chemistry Division, Code 6120
Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5000

Professor Jerald S. Bradshaw
Department of Chemistry
Brigham Young University
Provo, UT 84602
R&T Code 413p002

Professor Ronald Breslow
Department of Chemistry
Columbia University
New York, NY 10027
R&T Code 413p005

Dr. Duncan W. Brown
Advanced Technology Materials, Inc.
520-B Danbury Road
New Milford, CT 06776

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907

Professor Steven L. Buchwald
Department of Chemistry
Massachusetts Institute of Tech
Cambridge, MA 02139

Professor Cynthia J. Burrows
Department of Chemistry
State University of New York at
Stony Brook
Stony Brook, NY 11794-3400

Dr. Roque J. Calvo
Executive Secretary
The Electrochemical Society
10 South Main Street
Pennington, NJ 08534-2896

Professor Peter Chen
Department of Chemistry
Harvard University
Cambridge, MA 02138

Professor N. John Cooper
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Professor Anthony W. Czarnik
Department of Chemistry
Ohio State University
120 West 18th Avenue
Columbus, OH 43210-1173

Professor Peter Dervan
Department of Chemistry
California Institute of Technology
Pasadena, CA 91125

Professor Francois N. Diederich
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles, CA 90024

Professor Dennis A. Dougherty
Department of Chemistry
California Institute of Technology
Pasadena, CA 91125

Professor Kenneth M. Doxsee
Department of Chemistry
University of Oregon
Eugene, OR 97403

Dr. Regis J. Ebner, Jr.
Director of Finance
Materials Research Society
9800 McKnight Road, Suite #27
Pittsburgh, PA 15237

Professor Margaret C. Etter
Department of Chemistry
University of Minnesota
207 Pleasant Street, S.E.
Minneapolis, MN 55455

Professor Wilmer K. Fife
Department of Chemistry
Indiana University
1125 East 38th Street
P.O. Box 647
Indianapolis, IN 46223

Professor Samuel H. Gellman
Department of Chemistry
University of Wisconsin
Madison, WI 53706

Professor Andrew D. Hamilton
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Prof. Mark J. Hampden-Smith
Department of Chemistry
University of New Mexico
Albuquerque, NM 87131

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Dr. Kelvin Higa
Chemistry Division
Research Department
Naval Weapons Center
China Lake, CA 93555

Professor Kenneth D. Karlin
Merryman Hall 146
The Johns Hopkins University
34th & Charles Streets
Baltimore, MD 21218

Professor Arthur E. Martell
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

Professor Thomas J. McCarthy
Department of Polymer Science
University of Massachusetts
Room 701 Graduate Research Center
Amherst, MA 01003
R&T Code 400x015

Dr. Stephen W. McElvany
Code 6113, Chemistry Division
Naval Research Laboratory
Washington, DC 20375-5000

Professor Lisa McElwee-White
Department of Chemistry
The Leland Stanford Junior Univ.
Stanford, CA 94305

Professor Theodore G. Pavlopoulos
Naval Ocean Systems Center
Code 521 (B-111)
San Diego, CA 92152-5000

Professor William S. Rees, Jr.
Chemistry Division
The Florida State University
Tallahassee, FL 32306-3006

Professor Peter Schultz
Department of Chemistry
University of California
Berkeley, CA 94720
R&T Code 415j005

Dr. Alok Singh
Ctr. for Bio/Molec. Science Eng.
Department of the Navy
Naval Research Lab., Code 6090
Washington, DC 20375-5000

Dr. Michael L. Sinnott
University of Bristol
School of Chemistry
Cantock's Close
Bristol, England BS8 1TS

Dr. Timothy M. Swager
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104-6323

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706

Professor Jeffrey D. Winkler
Department of Chemistry
The University of Chicago
5735 S. Ellis Avenue
Chicago, IL 60637

Professor Jeffrey D. Zubkowski
Department of Chemistry
Jackson State University
P.O. Box 17910, 1400 Lynch St.
Jackson, MS 39217